Delocalized electrons: conductivity and superconductivity

Haigang Lu*

Institute of Theoretical and Computational Chemistry,
College of Chemistry, Peking University, Beijing 100871, China
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When wavefunction of crystal was projected out in atomic basis, we found that electrons of s orbital had localization-delocalization duality, and the ones of p and d orbital were only localized in three dimensional crystal lattice. The existence of s type delocalized electrons is based on three dimensional ordering of electron density in metals. Then charge carriers of metals for conductivity are just such delocalized electrons so that the ones for superconductivity are electron pairs of s wave. This way could also be generalized to two dimensional case for CuO_2 plane of cuprate superconductor to explain its phase diagram qualitatively. We also gave some *ab initio* explain for Hubbard model.

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I. INTRODUCTION

Density functional theory(DFT) have success to predict almost all of structure of molecular and crystal, but band theory of DFT explains conductivity partly. The classical theory on conductivity is based on band structure of Bloch's theorem, in which charge carriers are electrons excited from valence bands to conduction bands or occupied in partially filled band. But it fails to explain the poor conductivity of Mott insulators[1] such as CoO, MnO, CuO, which have half-filled band structure, while CuO is the principle component of cuprate high temperature superconductor. So, a unified theory of conductivity on metals and Mott insulators is one of keys for high temperature superconductivity.

It became practicable after we found the relations between delocalization of electrons and types of atomic orbitals when projecting bands of crystal to atomic orbitals, because delocalized electrons was just electron mobility[2] with respect to their original ions in lattice. Then, charge carriers will be not excited electrons, but the delocalized ones near Fermi surface. Certainly, this way is still based on the band structure of Bloch's theorem.

This paper includes five parts: First we elaborated that Slater type orbital(STO) was the best function to project out the atomic components from plane wave function, in which ζ was the best parameter to represent the degree of delocalization in three dimensions. Secondly, the localization-delocalization duality of s electrons and localization of p and d ones are found, from which conductivity and Hubbard model is explained. Thirdly, the mechanism of superconductivity is given based on the barrier between localization and delocalization and the phase diagram[3] of cuprate superconductors is explained qualitatively. Fourthly, we will use percolation theory[4] to connect the microscopic and macroscopic mechanism of (super)conductivity. At last, we will end this paper by a conclusion.

II. OPTIMIZED PSEUDO ATOMIC ORBITAL

To give band structure of crystal, there are two widely used methods, plane waves and atomic orbitals. What we used is the former in addition to *ab initio* pseudopotential[5], and these provide a very successful scheme to calculate the ground state properties of crystal. But only atomic basis is adequate to analysis atomic properties of crystal. We have to project out the corresponding pseudo atomic orbitals[6] from the bands of plane wave calculations using pseudopotential.

For posterior analysis of atomic properties, the best pseudo atomic orbital is single Slater type orbital $\chi_{nlm}(\boldsymbol{r}) = N_s R_n(\zeta, r) Y_{lm}(\theta, \phi)$[7], where N_s is the normalization constant, $Y_{lm}(\theta, \phi)$ is the spherical harmonics, $R_n(\zeta, r) = r^{n-1} \exp(-\zeta r)$ is the radical function and ζ is a parameter of n and l. There are four reasons for STO: (1) single ζ-optimised STOs can almost be equivalent to plane wave basis when atoms are far enough each other, (2) single STOs have the well-defined physical mean, where the n is main quantum number, l is angular momentum quantum number and m is magnetic quantum number, (3) there is a single variable ζ to indicate the transformation of atomic orbitals between isolated atom and atom in crystal after optimised, (4) ζ is also a parameter to indicate the degree of delocalization of electrons with respect to the original ions, because the classical radius of atomic orbital is n/ζ so that the smaller ζ, the larger radius, the more delocalization.

Criterion should be given to optimise the variable ζ. In projecting, the quality of an atomic basis is quantified by its ability to represent those eigenstates of plane wave basis, i.e., the completeness of crystal orbitals in subspace spanned by the atomic basis, which is always less than 100%. From the Rayleigh-Ritz minimal principle, energy of an electronic ground state $E = \min_\psi(\psi, H\psi)$, where H is Hamiltonian and ψ is a normalized trial function for the given number of electrons N. After projecting to a single STO of one variable ζ, the above formula will become

*Electronic address: luhg@pku.org.cn

$E = \min_\zeta[\psi(\zeta), H\psi(\zeta)]$ so that the energy of system is a function of ζ and the less incompleteness of atomic basis, the lower trial energy of system. Then we could analyse electron state by the relation of incompleteness or energy and ζ of STO.

The electronic structures of supercell are calculated using *ab initio* plane-wave code CPMD3.9.1[8] of density functional theory, where sizes of supercell are larger than 1nm×1nm×1nm. The exchange-correlation functional was Perdew-Burke-Ernzerhof[9] ones of the generalised gradient approximation. The interaction of ion-electron was described by Goedecker pseudopotential[10] with cutoff energy of plane-wave 40 or 100 Rydberg for $4s$ or $3d$ and $2p$ shell respectively and shell of valence electrons is as few as possible. The data of normal crystal structures come from experiment.

FIG. 1: Some typical graphs of incompleteness of atomic orbital versus ζ of STO. ζ is in atomic unit and the a in (c) is lattice parameter of supercell.

III. LOCALIZATION AND DELOCALIZATION, HUBBARD MODEL

Fig. 1a and 1b gave some typical graphs of incompleteness of atomic basis versus ζ of STO in different crystal structure: s type orbitals in body-centred cubic (K), face-centred cubic (Cu) and hexagonal close-packed (Zn) lattice, d type ones in body-centred cubic (Cr) and face-centred cubic (Cu) lattice, p type one in diamond (C). From these figures we could find that, there must be two minimums at large and small ζ separated by a group of barriers for electrons in s orbital, and only one minimum for ones in p and d orbitals at large ζ, so that electrons of s orbitals have localization-delocalization duality, while ones of p and d orbitals only is localized in three dimensional crystal lattices. Localized electrons always appear in lattice and bond atoms one by one so that solids is solid, while delocalized electrons appear in metals to form long-range bonds so that metals have extensibility. By the way, the mean of "duality" here is analogous with the wave-particle duality in quantum mechanics for s type STO of $\zeta = 0$ is just plane wave and the one of $\zeta = \infty$ just point particle.

Because localization-delocalization duality of atomic orbitals is a phenomena of electronic structure of crystal on *ab initio* calculation, we will investigate the origin of minimums and barriers. Fig. 2 is graph of incompleteness of $4s$ orbital of Cu in four atoms cell, where the insets above the curve are corresponding distribution of orbitals in two dimensional section. In these insets, the right and left are localized and delocalized $4s$ orbitals respectively, which give sketch of electron distribution in crystal, and the middle is $4s$ orbitals in barrier, in where electron density is the lowest. From the view of wave, the electronic density in crystal is variable periodically in three dimensions so that the s wave, an isotropic wave in three dimensions could spread from near to far away original ion, but it will undergo a scatter just when leaving the original ion. To p, d and f wave, there are two types of symmetry: p, d_{z^2}, f_{z^3} waves are isotropic only
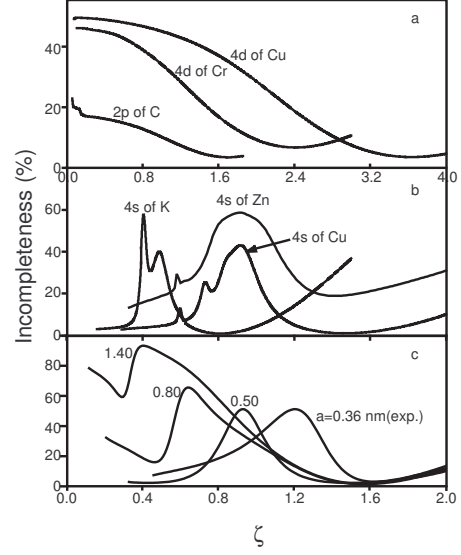
in two dimensions so that the periods of electron density are not commensurable between these two dimensions and the other dimension; the others is anisotropic, so that the periods of electron density is not commensurable among all of three dimensions. Then p, d and f waves would undergo scatter continuously not to spread away from the localized orbitals. This localization of p, d and f wave in three dimensions gives one instance for Anderson localization of disordering[11]. Now we conclude that only waves whose symmetry is fit with medium could spread, that is to say, s wave could spread in three dimensional lattice and p, d_{z^2} and f_{z^3} wave could spread in two-dimensional sheet.

This relation between delocalization of electrons and types of wave has a far-reaching consequences that charge carriers is s wave in three dimensional conductor such as metal conductors and superconductors, and p, d and/or f wave in two dimensional conductors such as graphite, organic conductors and cuprate superconductors. In Mott insulators such as CoO, MnO, CuO, electrons near Fermi surface belong to $3d$ of transition metals and $2p$ of O so that there are not s but d and/or p type charge carriers. Then Mott insulators are insulators in three dimension. The above also explain experimental facts that charge carriers are s waves in metal superconductors and d waves in cuprate superconductors[12], but the d wave of Cu in our theory is not $d_{x^2-y^2}$ but d_{z^2}, and $2p$ of O could also be delocalized to contribute to charge carriers in CuO_2 plane and direction perpendicular to this plane. We conjectured that $d_{x^2-y^2}$ symmetry of charge carrier was just some linear combination of $2p_z$ orbitals of O in CuO_2 plane.
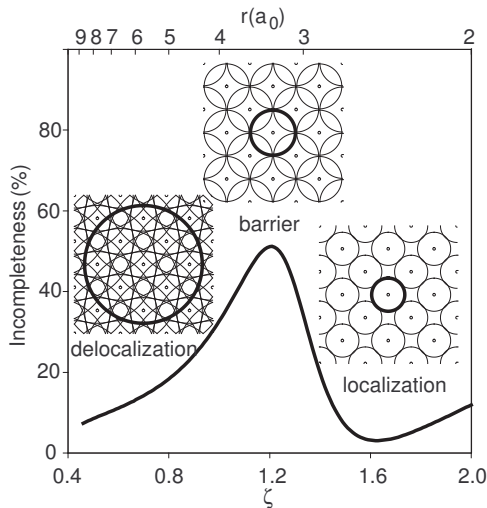
FIG. 2: Graph of incompleteness of $4s$ orbital of Cu versus ζ and radius of STO and corresponding distribution of orbitals on two dimensional section. The a_0 for radius is Bohr radius 0.0529nm

When do the delocalized electrons occur to transit Mott insulators to conductors or superconductors? That is to say, when the localized orbital, the fundamental state in bond need to be delocalized? We knew that metallic bond is unsaturated bond of s orbitals, and π bond in organic conductors is also unsaturated bond of p orbitals relative to σ bond, so that electron deficient of bond is the common characteristic of delocalization of bond as well as of electrons. So the transition of Mott insulator-metal comes from electron deficient of bond, in which the doped cuprate superconductors are just some instances. To clarify the change of localization-delocalization duality in Mott metal-insulator transition, we investigate an ideal Mott transition: the delocalization of $4s$ of Cu for different distance of atoms in four atoms cell(Fig. 1c), in which more energy for delocalization of electrons is needed as lattice parameter become large. And this difference of energy between delocalization and localization is just as Hubbard energy in Hubbard model[1]. The lattice parameter $a = 1.4$nm means the corresponding "metal" has poor conductivity for the minimum distance of atoms is large to 1.0nm. And crystal of $a = 0.36$nm is just true copper metal. From above we concluded that the distance larger, the more incompleteness of delocalization, the less conductivity so that metal transited to insulator.

IV. SUPERCONDUCTIVITY

As transforming the incompleteness of projecting to energy of system, graphs of incompleteness versus ζ become two electronic states separated by a energy barrier, and these two states can transition each other by electron tunneling. When delocalized and localized electrons form bonds by electron pairing of different spin, there are three possible kinds of electron pair: hybrid $\alpha_L\beta_D$ and $\alpha_D\beta_L$, localized $\alpha_L\beta_L$ and delocalized $\alpha_D\beta_D$ pair, where α and β are spin of electrons and subscripts L and D represent localized and delocalized state respectively. In high temperature, almost all of the electrons have enough energy across the barrier so that only hybrid pairs can exist. As the temperature falls, some of electrons in lowest energy of states are not able to transit and are delocalized or localized, then delocalized and localized pairs will occur because of bonding, which had been supported by two-component electrons in cuprate superconductors[13]. It shows that the barrier between localization and delocalization determines the temperature of pairing of charge carriers, even transition temperature of superconductivity in metals.

The energy barriers in metals are very low because their electron density is highly homogeneous in real space so that the temperature for prohibiting transition of some electron pairs should be very low, while in cuprate superconductors the barriers are high because their electronic structure is much more prone to inhomogeneity[14]. One of keys of cuprate high temperature superconductivity is its "phase diagram"(Fig. 3c). To explain this, we should first determine the delocalized states of electrons near Fermi surface as Mott insulators are doped to transit to metals (Fig. 3b), which could be deduced from Fig. 1c. The pseudogap in normal state of cuprate superconductors would come from the imbalance of electrons of localized and delocalized state. In high temperature, the difference of energy between localized and delocalized states are negligible so that partition of electrons in two states is duality and Fermi surface fill in, but as temperature falls below temperature of pseudogap, this difference of energy would dominate partition, then there are more localized electrons than delocalized ones and no enough electrons for Fermi surface so that this surface will be broken (Fig. 3a)[15]. So, pseudogap does correspond with a phase transition with broken Fermi surface. On the other hand, more doping produces more itinerant electrons and reduces inhomogeneity so that the barrier will decreases as doping, so T_c will rise first and then drop. In underdoped side, there is no enough carriers and transition temperature T_c is dominated by hole concentration, and in overdoped side, the energy barrier is low so that T_c is determined by energy barrier for delocalized state.

V. PERCOLATION

For superconductivity of cuprate superconductors, there is a similar critical fraction 0.05 of hole concentration, which could be deduced from the delocalized radius of electron and percolation theory. Percolation theory is the bridge between microscopic and macroscopic mechanism of (super)conductivity, in which the delocalized orbitals were thought of (super)conductor spheres and lo-
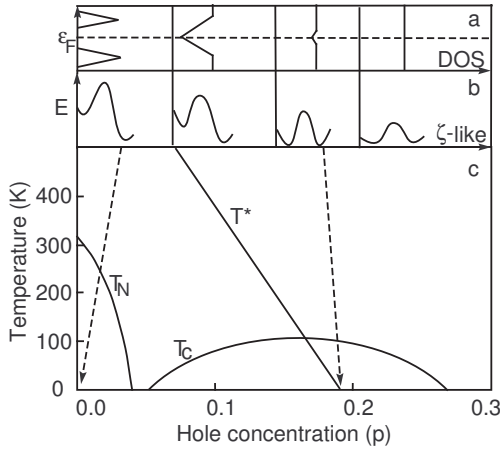
FIG. 3: Schematic phase diagram of cuprate superconductors (c) and corresponding schematic diagrams for density of state(DOS) (a) and delocalization of orbitals (b) near Fermi surface. T_N is the Neel temperature for three dimensional antiferromagnetic state, T_c the transition temperature of superconductivity and T^* the temperature below which the normal-state pseudogap opens, ζ-like is the corresponding parameter of delocalization in two dimensional cases.

calized ones insulator spheres. Because the radius of delocalized orbital is much larger than of localized one, we should use the (super)conductor sphere as unit to calculate thresholds for percolation. Once the fraction of carriers exceeds the corresponding threshold, insulators will transit to metal, or electron pairs will cohere to form superconductors. For example, in two-dimensional sheet of cuprate superconductivity, it is less than $0.6/3^2 = 0.067$, where 0.6 is threshold of square in site percolation, 3 is theoretical minimum for radius of delocalization divided by one of localization, and 2 comes from dimensionality. This threshold is compare with our critical fraction 0.05 in phase diagram of cuprate conductors.

In three dimensional metals, for example in face-centred cubic(FCC) copper, the threshold of (super)conductivity is less than $0.2/5^3 = 0.0016$, where 0.2 is threshold of site percolation for FCC lattice, 5 is minimum for radius of delocalization divided by one of localization in Fig. 1b, and 3 comes from dimensionality. It is compare with 0.0001[16], fraction of charge carriers in metal superconductivity. From above instances we knew that thresholds of percolation of (super)conductivity were very sensitive to the dimensionality of (super)conductors and were very small in three dimensional case so that electron pairing and its condensation of coherence occur almost simultaneously, while the critical fraction in two dimensional sheet of cuprate superconductor is rather large so that electrons pairing should occur before its condensation of coherence distinctly. So we predict that superconductors at room temperature should be ionic compound of delocalized s electrons because they should have high barrier between delocalization and localization and small thresholds of percolation in three dimension, which may find from the other end of $3d$ transition metal oxide such as Sc_2O_{3-x}, TiO_{2-x} or V_2O_{5-x}, because their $4s$ and $3d$ orbitals are both near Fermi surface to form s type conductors when insulators transit to conductors.

VI. CONCLUSION

We found the localization-delocalization duality of s electrons in metals, from which we unified the theory of conductivity for metals, Mott insulators and organic conductors. The phase diagram of cuprate superconductors also be explained by ideal Mott insulator-metal transition qualitatively. We also predicted that higher temperature superconductor might be ionic compound with delocalized s electrons.

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